

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 January 2003 (03.01.2003)

PCT

(10) International Publication Number
WO 03/000628 A1

(51) International Patent Classification: C07C 2/32

VAN ZON, Arie [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).

(21) International Application Number: PCT/EP02/06739

(22) International Filing Date: 18 June 2002 (18.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01305353.3 20 June 2001 (20.06.2001) EP

(71) Applicant (for all designated States except US): SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR
The Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): DE BOER, Eric,
Johannes, Maria [NL/NL]; Badhuisweg 3, NL-1031 CM
Amsterdam (NL). DEULING, Hendrikus, Hyacinthus
[NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).
VON HEBEL, Klaas, Lambertus [NL/NL]; Badhuisweg
3, NL-1031 CM Amsterdam (NL). RUISCH, Bart, Johan
[NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PREPARATION OF OLIGOMERS

(57) Abstract: Process for the oligomerization of one or more olefinically unsaturated monomers comprising three or more carbon atoms, at least one of these monomers consisting of a C₃ to C₃₀ aliphatic mono-olefin, which process comprises reacting the olefinically unsaturated monomer(s) under oligomerization conditions in the presence of an effective amount of a catalyst system based on, a) a specific titanium bisamide compound or its dimer; b) one or more activating cocatalysts comprising at least one boron atom; and optionally, but in any event if the titanium bisamide compound or its dimer comprise halogen; c) one or more aluminium alkyls or alumoxanes. A mixture of homo-oligomers of propylene is obtainable by the above process, which mixture comprises oligomers of propylene based on up to 20 propylene molecules, wherein at least 50 mole % of the oligomer chains have a terminal vinyl group.



WO 03/000628 A1

- 1 -

PROCESS FOR THE PREPARATION OF OLIGOMERS

The present invention relates to a process for the preparation of oligomers from one or more olefinically unsaturated monomers comprising three or more carbon atoms using a catalyst system based on a specific titanium
5 bisamide compound. The invention also relates to specific propylene homo-oligomers, which can be obtained by this process.

Bisamido transition metal compounds are known to be active as catalysts for polymerizing α -olefins. For
10 instance, International patent applications Nos. WO-92/12162 and WO-96/27439 both disclose the use of such compounds in conjunction with alumoxanes or boron compounds as catalysts for polymerizing ethylene and propylene. In both patent specifications only zirconium and hafnium
15 bisamide compounds are exemplified.

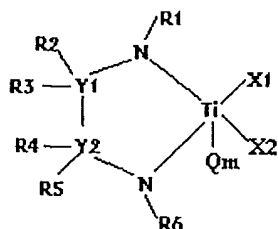
Copending European patent application No. 00203330.6 discloses the use of catalyst systems obtainable by contacting a titanium bisamide compound, one or more
20 activating boron-containing cocatalysts and possibly one or more aluminoxanes or aluminium alkyls in the homopolymerization of ethylene and copolymerization of ethylene with higher olefins.

The present invention relates to a process for the oligomerization of one or more olefinically unsaturated
25 monomers comprising three or more carbon atoms using the catalyst system described in the aforesaid copending European patent application No. 00203330.6.

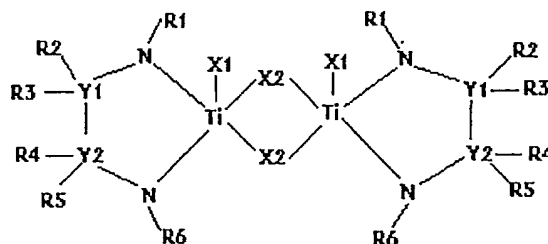
- 2 -

Accordingly, the present invention relates to a process for the oligomerization of one or more olefinically unsaturated monomers comprising three or more carbon atoms, at least one of these monomers consisting of a C₃ to C₃₀ aliphatic mono-olefin, which process comprises reacting the olefinically unsaturated monomer(s) under oligomerization conditions in the presence of an effective amount of a catalyst system based on

- (a) a titanium bisamide compound of general formula (I) or its dimer of general formula (II)



(I)



(II)

wherein:

Y¹ and Y² independently represent silicon (Si), germanium (Ge) or tin (Sn);

X¹ and X² independently represent a substituted or unsubstituted hydrocarbon group, in which one or more

- 3 -

of the carbon atoms may be replaced by a Si atom,
while in formula (I) X^1 and X^2 may also independently
represent hydrogen or halogen or together form a ring
structure; and

5 R^1 , R^2 , R^3 , R^4 , R^5 and R^6 independently represent
hydrogen, halogen or a substituted or unsubstituted
hydrocarbon group;

Q represents a neutral Lewis base; and

m is 0 or 1;

10 (b) one or more activating cocatalysts selected from the
group consisting of

(i) compounds of formula U^+Z^- , wherein U^+ represents a
cation capable of reacting irreversibly with one
or more of the substituents X^1 and X^2 of the
15 compound of formula (I) or (II) and Z^- represents
a compatible non-coordinating anion comprising at
least one boron atom; and

(ii) neutral strong Lewis acids comprising at least
one boron atom; and

20 optionally, but in any event if in the compound of
formula (I) or (II) at least one of X^1 or X^2 represents
halogen:

(c) one or more aluminium alkyls or alumoxanes.

25 It was surprisingly found that when using the titanium
bisamide catalyst-based catalyst system defined above for
polymerizing propylene a very high selectivity for vinyl
group-terminated polymer chains ($-CH=CH_2$) was attained,
whereas an extensive array of Group 4 metal-based catalyst,
including similar zirconium bisamide catalysts, under
30 identical conditions produce predominantly vinylidene-
terminated polymer chains ($-C(CH_3)=CH_2$). Furthermore, an

- 4 -

additional advantage of the present invention is that when C4 or higher olefins are used as monomer(s) the number of branches in the final oligomer molecule is less than when using the corresponding zirconium bisamide catalysts. Yet
5 another major advantage is that in the present process a high proportion of linear dimer molecules is formed. Such dimer molecules are, for instance, particularly useful as comonomers in the production of linear low density polyethylene. It was surprisingly found that the titanium
10 bisamide catalyst-based catalyst system defined above results in a higher proportion of dimers than would be expected in a normal oligomerization reaction obeying Schulz-Flory distribution, wherein the relative amounts of oligomer fractions are constant for two successive
15 fractions and thus formation of dimers is not normally favoured over trimers, tetramers, pentamers etc.

The expressions "oligomerization", "oligomers", "oligomerized" and words derived from any of these expressions as used throughout this specification cover
20 every reaction between two or more olefinically unsaturated monomer molecules, either the same or different, as well as any molecule resulting from such reaction up to a molecular weight of 10,000. Accordingly, the range of molecular weights covered ranges from 84 (i.e. two propylene
25 molecules) to 10,000. The expression "molecular weight" as used throughout this specification refers to the molecular weight as determined by gas chromatography and NMR.

The olefinically unsaturated monomers, which can be oligomerized in accordance with the present process, are
30 compounds comprising at least three carbon atoms and at least one olefinic bond, suitably at least one α -olefinic

- 5 -

bond. Compounds with internal olefin bonds may also be used, but are less suitable. Accordingly, suitable monomers include C₃ to C₃₀ aliphatic mono- α -olefins and dienes, such as 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 3,7-dimethyl-1,6-octadiene and 5-ethylidene-2-norbornene, as well as aromatic compounds containing one or more olefinically unsaturated substituents (e.g. styrene, divinylbenzene). The olefin monomers may also contain inert functional groups, such as silyl groups (e.g. trimethylsilyl). Preferred monomers, however, are the C₃ to C₃₀ aliphatic mono- α -olefins, more preferably the C₃ to C₁₂ aliphatic mono- α -olefins. In a preferred embodiment the process of the present invention comprises reacting one or more of these mono- α -olefins.

The titanium bisamide compound of formula (I) and its dimer of formula (II) can both be used as component (a) of the catalyst system. It is, however, preferred to use the compound of formula (I). In the titanium bisamide compound of formula (I) and its dimer of formula (II), the atoms Y¹ and Y² are preferably identical and represent Si.

The groups X¹ and X² are preferably selected from hydrogen, halogen, C₁-C₅ alkyl, 4-alkylphenyl, phenyl and benzyl. Examples of very suitably C₁-C₅ alkyl groups are methyl, ethyl, propyl and n-butyl. The groups X¹ and X² can also form a ring having from 4 to 8 members together with the titanium atom. Most preferably, X¹ and X² are the same and selected from halogen, methyl and benzyl groups.

The groups R¹, R², R³, R⁴, R⁵ and R⁶ are the same or different and are preferably selected from hydrogen, C₁-C₅ alkyl, trimethylsilyl, C₅-C₈ cycloalkyl, phenyl and benzyl. Suitable C₁-C₅ alkyl groups in this connection are methyl,

- 6 -

ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl and tert-amyl, while from the C₅-C₈ cycloalkyl groups cyclopentyl and cyclohexyl are preferred. In addition to the preferred options mentioned above, groups R¹, R², R³, R⁴, R⁵ and R⁶ may also represent other groups like dimethylphenyl, diisopropylphenyl, tri-tert-butylphenyl, diphenylethyl and triphenylmethyl. It was found that the best results are obtained when R¹ and R⁶ are groups, which provide steric hindrance to the Ti atom. Thus, bulky groups like tert-butyl and 2-phenyl-isopropyl are very suitable groups. In a very much preferred embodiment R², R³, R⁴ and R⁵ are methyl groups and R¹ and R⁶ are tert-butyl groups.

Q is a neutral Lewis base, which may (m=1) or may not (m=0) be present. Examples of suitable Lewis bases are diethylether, tetrahydrofuran, diethylaniline and dimethylaniline.

Preferred compounds of formula (I) and (II) are those wherein the groups Y¹, Y², X¹, X², R¹, R², R³, R⁴, R⁵ and R⁶ have the preferred meanings as indicated hereinbefore and m=0. The most preferred compounds of formula (I) are {1,2-bis(t-butylamide)-tetramethyldisilane} titanium dibenzyl {Me₂SiN-t-Bu)₂} Ti(CH₂Ph)₂ and {1,2-bis(t-butylamide)-tetramethyldisilane} titanium dichloride {Me₂SiN-t-Bu)₂} TiCl₂.

The bisamide compounds of formula (I) and (II) can be prepared by methods known in the art, more specifically as described in WO-96/27439 and Chem.Ber./Recl. (1997), 130(3), 399-403.

Component (b) of the catalyst system used in the process of the present invention is at least one activating cocatalyst selected from neutral strong Lewis acids

- 7 -

comprising at least one boron atom and compounds of formula U^+Z^- , wherein U^+ represents a cation capable of reacting irreversibly with one or more of the substituents X^1 and X^2 of the compound of formula (I) or (II) and Z^- represents a compatible non-coordinating anion comprising at least one boron atom, suitably a boron-containing bulky and labile anion which is non-coordinating under the reaction conditions applied. Suitable strong Lewis acids are those Lewis acids capable of extracting at least one of the radicals X^1 and X^2 from the compound of formula (I) or (II), thereby also contributing an anion Z^- . The anion Z^- must be capable of stabilising the active catalyst species resulting from the reaction between the compound of formula (I) or (II) with the activating cocatalyst and must be sufficiently labile in order to be replaceable by an olefinic substrate during the oligomerization reaction. Compounds of formula U^+Z^- are preferred cocatalysts.

In a preferred embodiment the cocatalyst is a compound of formula U^+Z^- , wherein U^+ represents a quaternary ammonium cation, preferably dimethylanilinium $[PhMe_2NH]^+$ or tri(n-butyl)ammonium $[Bu_3NH]^+$. U^+ may also represent a non proton-donating cation, in particular a metal cation like a silver ion or a triphenylcarbonium ion. Z^- suitably represents a borate anion of formula $[B(R^8)_4]^-$, wherein the groups R^8 independently represent hydrogen or halogen-substituted (most suitably fluorine-substituted) or unsubstituted C_1 - C_{10} alkyl, C_5 - C_8 cycloalkyl, phenyl, C_7 - C_{15} alkylaryl or C_7 - C_{15} arylalkyl groups. Specific examples include tetraphenyl borate $[B(C_6H_5)_4]^-$, tetrakis (pentafluorophenyl) borate $[B(C_6F_5)_4]^-$, tetrakis (3,5-bis-trifluoromethyl-phenyl) borate $[B(3,5-(CF_3)_2-C_6H_3)_4]^-$ and tetrakis (4-fluorophenyl)

- 8 -

borate $[B(4-F-C_6H_4)_4]^-$, of which tetrakis
(pentafluorophenyl) borate is most preferred. Furthermore,
 Z^- may contain multiple boron atoms, such as in carborates
like 1-carbodecarborate $[B_{11}CH_{12}]^-$. The preferred compounds
5 of formula U^+Z^- are those in which U^+ and Z^- have a
preferred meaning as indicated hereinbefore. A very much
preferred compound of formula U^+Z^- is dimethylanilinium
tetrakis (pentafluorophenyl) borate $[PhMe_2NH]^+ [B(C_6F_5)_4]^-$.

The boron-containing component (b) can be prepared by
10 methods known in the art, such as e.g. disclosed in WO-
96/27439.

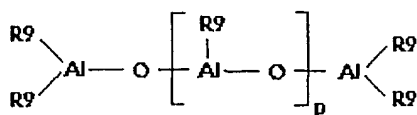
The catalyst system may in addition be based on one or
more aluminium alkyls or alumoxanes (component (c)). If in
the compound of formula (I) or (II) at least one of X^1 and
15 X^2 represents halogen, then this component (c) is anyhow
present; in that case it acts as alkylating agent. In
general, however, the presence of on one or more aluminium
alkyls or alumoxanes is advantageous, as they act as
scavengers for removing oligomerization poisons, such as
20 molecules containing N-, O-, S- or P-donor atoms.

Suitable aluminium alkyls are, for example, compounds
of the general formulas $H_xAlR^9_{3-x}$ or $H_yAl_2R^9_{6-y}$, wherein x and
y are (possibly non-integer) numbers ranging from 0 to 1
and the groups R^9 independently represent halogen, C_1 - C_{20}
25 alkyl or alkenyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20}
alkylaryl and C_7 - C_{20} arylalkyl groups with branched C_1 - C_{20}
alkyl and C_7 - C_{20} alkylaryl groups being preferred. Mixtures
of different aluminium alkyls can also be used.
Particularly preferred aluminium alkyl compounds are
30 trimethyl aluminium, tris(2,4,4-trimethylpentyl) aluminium,
tri-isobutyl aluminium, tris(2,3,3-trimethyl-butyl)

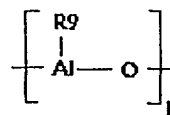
- 9 -

aluminium, tris(2,3-dimethyl-butyl) aluminium, tris(2-phenyl-propyl) aluminium, tris[2-(4-fluorophenyl)propyl] aluminium and tris[2-(4-chlorophenyl)-propyl] aluminium.

Suitable alumoxanes that can be used as component (c) may be linear alumoxanes of general formula (III) or cyclic alumoxanes of formula (IV)



(III)



(IV)

wherein R^9 has the meaning as described hereinbefore and p is an integer ranging from 3 to 40. These alumoxanes may be obtained by methods known in the art by reacting water with an aluminium alkyl of general formula $\text{H}_x\text{AlR}^9_{3-x}$ or $\text{H}_y\text{Al}_2\text{R}^9_{6-y}$ with the proviso R^9 is not halogen. In this case the molar ratio of Al to water may suitably range from 1:1 to 100:1. Suitable organometallic aluminium compounds are also those represented by formula (II) in EP-A-0 575 875 and those represented by formula (II) in WO-96/02580.

The amount in which the catalyst components are used may vary within broad limits. Typically, the molar ratio between components (a) and (b) of the catalyst system is in the range of from 0.1:1 to 5:1, preferably 0.2:1 to 2.5:1 and more preferably 0.3:1 to 1.1:1. Component (c), if present, is suitably used in such amount that the molar ratio between the aluminium in component (c) and the Ti in component (a) ranges from 10:1 to 10,000:1, preferably 20:1 to 5000:1 and more preferably 20:1 to 1000:1.

- 10 -

The catalyst system may be used as a homogeneous catalyst by adding the catalyst components to the liquid reaction medium, so that the active catalyst will be formed in situ. Alternatively, the catalyst system may be supported on a solid inert support material, thereby also enabling the oligomerization reaction to take place in the gas phase. If used on an inert support material, the catalyst components are deposited on the support material, e.g. by impregnation with one or more suitable impregnating solutions. Suitable support materials include refractory oxides such as silica, silica-alumina, alumina, titania, zirconia and magnesia, as well as zeolitic carriers. Furthermore, olefin polymers or prepolymers may be used as support materials. Examples include polyethylenes, polypropylenes and styrene/divinylbenzene copolymers.

The process of the present invention can be carried out in the liquid phase or in the gas phase. If carried out in the liquid phase the reactant monomers and oligomer formed may provide the reaction medium, but alternatively an inert hydrocarbon solvent may be used. Suitable solvents include aromatic hydrocarbons like toluene or aliphatic hydrocarbons like pentane, hexane, heptane, isobutane or cyclohexane.

The conditions under which the oligomerization of the present invention is carried out are not particularly critical and may vary within broad limits. Typically, however, reaction temperatures will be in the range of from -100 °C to +200 °C, preferably 0 °C to 100 °C and more preferably 10 °C to 90 °C. The oligomerization pressure is typically in the range of from 0.5 to 100 bara, preferably 1 to 50 bara.

- 11 -

The process of the present invention is suitable for preparing homo-oligomers of propylene and higher mono- α -olefins, particularly up to C₃₀ olefins, and co-oligomers of such olefins with each other or with other olefinically unsaturated monomers mentioned hereinbefore. The length of the oligomer chain prepared may start from two monomer molecules and suitably does not exceed twenty, more suitably ten and most suitably five monomer molecules. Nevertheless, longer chains may be prepared, but the molecular weight will anyhow not exceed 10,000.

Preferred oligomers to be prepared in accordance with the present invention are homo-oligomers of C₃ to C₃₀ aliphatic mono- α -olefins, more preferably C₃ to C₁₂ aliphatic mono- α -olefins, having a molecular weight up to 10,000, preferably up to 5000 and more preferably up to 1000. Particularly preferred oligomers are homo-oligomers of propylene, 1-butene, 1-pentene, 1-hexene, 1-decene and 1-dodecene. However, co-oligomers of propylene with other C₄ to C₁₂ mono- α -olefins can also be very suitably prepared in the process according to the present invention.

It was surprisingly found that when using the titanium bisamide catalyst system of the present invention and propylene as the sole monomer, a very high proportion of the oligomer chains formed is terminated with a vinyl group (i.e. -CH=CH₂). By means of comparison: structurally corresponding zirconium bisamide catalyst systems as disclosed in WO-96/27439 result in a much higher proportion of vinylidene-terminated propylene oligomer chains (i.e. - (CH₂)C=CH₂). The advantage of having a vinyl end-group is that the oligomer can be used as comonomer in other polymerization reactions, such as in the preparation of

- 12 -

linear low density polyethylene. This is not possible with oligomer molecules having a vinylidene end group.

As indicated hereinbefore, further advantages of the present process are that a very high proportion of linear dimers is formed instead of dimers containing a branch. If propylene is used as the monomer a substantial part of these dimers will have a vinyl end group. If a C4 or higher mono- α -olefins is used as monomer, the linear dimer formed will have an internal olefinic bond. This surprising finding is thought to be the result of the very specific termination mechanism caused by the titanium bisamide catalyst used.

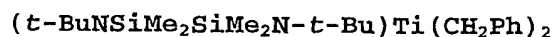
Accordingly, in a further aspect the present invention relates to a mixture of homo-oligomers of propylene obtainable by the process of the present invention, which mixture comprises oligomers of propylene based on up to 20, preferably up to 10 and more preferably up to 5, propylene molecules, wherein at least 50 mole% of the oligomer chains have a terminal vinyl group.

The invention also relates to homo-oligomers of

The invention will now be illustrated by the following examples without limiting the scope of the invention to these particular embodiments.

Examples

Example 1 **Preparation of**



To a solution of $(t\text{-BuHNSiMe}_2\text{SiMe}_2\text{NH-}t\text{-Bu})$, (2.5 g, 9.6 mMole) in 25 ml of hexane, 12.6 ml of 1.6 M $n\text{-BuLi}$ /hexane solution (20.2 mMole) was added slowly at -78°C . The reaction mixture was stirred for 1.5 hours while slowly

- 13 -

warming to room temperature. The resulting off-white precipitate was decanted and the washed with 10 ml of hexane. After removal of the hexane layer and drying the solids, 2.5 g of product was isolated.

5 $^1\text{H-NMR}$ (thf- d_8): δ 1.11, (s, 18H, CMe_3), 0.04 (s, 12H, SiMe_2).

B. (t-BuNSiMe₂SiMe₂N-t-Bu)TiCl₂ [2]

To a stirred solution of TiCl_4 (5.3 g, 5.5 mMole) in 25 ml of toluene was added slowly a suspension of [1] (1.5 g, 5.5 mMole) at -78°C . The reaction mixture is allowed to
10 warm to room temperature slowly and stirred for another 4 hours. Subsequently the volatiles were evaporated and the dark residue extracted twice with 15 ml of hexane. The combined hexane layers were cooled to -40°C affording a crystalline product. After removing the mother liquor by
15 syringe, the remaining crystals were washed with 5 ml of diethyl ether, dried under vacuum, and subsequently isolated. Yield 0.14 g of [2].

$^1\text{H-NMR}$ (C_6D_6): δ 1.44 (s, 18H, CMe_3), 0.08 (s, 12H, SiMe_2)

C. (t-BuNSiMe₂SiMe₂N-t-Bu)Ti(CH₂Ph)₂ [3]

20 To a stirred suspension of [2] (0.1 g, 0.26 mMole) in 5 ml of diethyl ether were added 5 ml of a 1M solution of PhCH_2MgCl (0.53 mMole) in diethyl ether at -78°C . After warming the solution to room temperature, the reaction
25 mixture was stirred for another 2 hours and subsequently all volatiles were evaporated off under vacuum. The remaining residue was extracted with 1.5 ml of hexane and the resulting hexane solution cooled overnight to -40°C . The resulting crystalline material was isolated after drying under vacuum. Yield 25 mg of [3].

30 $^1\text{H-NMR}$ (C_6D_6): δ 7.08 (t, 4H, *m*-Bz), 6.94 (t, 4H, *o*-Bz), 6.92 (t, 2H, *p*-Bz), 2.89 (s, 4H, TiCH_2) 1.52 (s, 18H, CMe_3), 0.08

- 14 -

(s, 12H, SiMe₂).

Example 2

Propene oligomerization in solution was carried out in a 1-litre steel autoclave equipped with jacket cooling with a heating/cooling bath and a turbine/gas stirrer. In order to remove traces of oxygen from the reactor, it was evacuated overnight at <0.1 mbara, at 70 °C. The temperature was then decreased to 50 °C and the autoclave was pressurized with nitrogen (4-5 bara). Subsequently, the reactor was scavenged with a solution of tetra-iso-butyl alumoxane (TIBAO) (300 mg) in iso-octane (140 g) and stirring was applied for 30 minutes. The reactor contents were discharged via a tap in the base of the autoclave. The reactor was evacuated to 4 mbara and loaded with 243 g of iso-octane as solvent and 2 g of n-hexylbenzene as an internal GC standard; the reactor was heated to 70 °C, pressurized with propylene and equilibrated for 15 minutes. Subsequently, [(t-BuNSiMe₂SiMe₂N-t-Bu)TiCH₂Ph⁺][B(C₆F₅)₄⁻] was prepared *in situ* by reaction of [3] (0.026 mMole) with 0.026 mMole [PhNMe₂H⁺][B(C₆F₅)₄⁻] (DANFABA) in toluene and added to the reactor using a catalyst injection device. The reaction was allowed to proceed for 1 hour after which the reaction was terminated by venting rapidly excess propylene, removal of the reactor contents via the base tap, and exposing the obtained liquid product to air. The reaction products obtained were characterized by means of GC and NMR.

From the GC and NMR analyses followed that 125 g of propene oligomers were formed. For the C₆-fraction the following olefins have been identified by GC: Hexene-1 (56% by weight), *cis*-hexene-2 (24%), *trans*-hexene-2 (8%),

- 15 -

4-methylpentene-1 (8%), *cis*-4-methylpentene-2 (3%), remainders (1%). The C₉-fraction contained 5-methyloctene-1 (52%). The oligomers did not contain vinylidene-terminated (R-C(CH₃)=CH₂) olefins in more than trace amounts.

5 Example 3

Propene oligomerization in liquid propylene at 50°C was carried out in a 5-litre autoclave, dried and scavenged prior to use, containing 1600 g of liquid propene and 3.0 mMole TIBAO. Catalyst used was made *in situ* by stirring
10 11.4 μMole of [3] with an equimolar amount of DANFABA for 20 minutes in 20 ml of toluene containing 0.1-0.2 mMole of TIBAO. Using a injection system, the catalyst was introduced in the reactor. The reaction was stopped after 60 minutes and the liquid contents of the reactor analysed.

15 The yield of the reaction was 352 g of propene oligomers of which the C₆ fraction consisted of hexene-1 (78%), *cis*-hexene-2 (10%), *trans*-hexene-2 (3%), 4-methylpentene-1 (7%), *cis*-4-methylpentene-2 (1%), remainders (<1%). The C₉-fraction contained
20 5-methyloctene-1 (75%). The average molecular weight of the product was 224. The oligomers did not contain vinylidene-terminated (R-C(CH₃)=CH₂) olefins in more than trace amounts.

Example 4

25 Propene oligomerization in liquid propylene at 70°C was carried out in a 5-litre autoclave, dried and scavenged prior to use, containing 1600 g of liquid propene and 3.0 mMole TIBAO. Catalyst used was made *in situ* by stirring
30 20.5 μMole of [3] with an equimolar amount of DANFABA for 20 minutes in 20 ml of toluene containing 0.1-0.2 mMole of TIBAO. Using a injection system, the catalyst was

- 16 -

introduced in the reactor. The reaction was stopped after 45 minutes and the liquid contents of the reactor analysed.

The yield of the reaction was 260 g of propene oligomers of which the C₆ fraction consisted of hexene-1 (76%), *cis*-hexene-2 (11%), *trans*-hexene-2 (4%), 4-methylpentene-1 (8%), *cis*-4-methylpentene-2 (1%), remainders (<1%). The C₉-fraction contained 5-methyloctene-1 (75%). The average molecular weight of the product was 266. The oligomers did not contain vinylidene-type (R-C(CH₃)=CH₂) olefins in more than trace amounts.

Comparative example 1

[(*t*-BuNSiMe₂SiMe₂N-*t*-Bu)ZrCH₂Ph⁺][B(C₆F₅)₄⁻], [3-Zr], was prepared according to a procedure similar to that described in WO-96/27439.

[3-Zr] was reacted with [Ph₃C⁺][B(C₆F₅)₄⁻] and excess propene in bromobenzene at 25°C for 3 hours in a small glass reactor at 1 bar. NMR analysis of the products showed the formation of *a*-tactic propene oligomers with the characteristic unsaturated -(CH₃)CH=CH₂ end-group.

Comparative example 2

To a 25 ml autoclave dried and evacuated prior to use, (*t*-BuNSiMe₂SiMe₂N-*t*-Bu)Zr(CH₃)₂ (0.03 mMole) which was reacted with an equimolar amount of B(C₆F₅)₃ dissolved in 10 ml of toluene, was added. Subsequently the autoclave was charged with 6.5 bar of propene and the reaction allowed to progress for 1 hour.

Analysis of the reactor contents showed the formation of hexenes (1 isomer), nonene (1 isomer), and higher propene oligomers. The hexene isomer was 2-methylpentene-1, i.e. the propene dimer with the characteristic unsaturated

- 17 -

- (CH₃)CH=CH₂ end-group.

Example 5

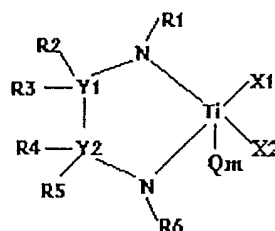
To a solution of pentene-1 (25 ml, dried over molsieves) in *iso*-octane (60 ml) containing 160 mg of
5 scavenger TIBAO, a solution containing a mixture of 29 mg of [3], 49 mg of DANFABA, and 90 mg of TIBAO in 5 ml of toluene was added at room temperature in a glovebox. The reaction was stopped after 90 minutes by filtration of the mixture over Al₂O₃ to kill and remove the catalyst and its
10 decomposition products. The resulting mixture was analysed and characterized by NMR and GC and found to contain pentene-1 oligomers with an average degree of polymerization between 5 and 6. The dimer fraction was shown to be a mixture of approximately equal amounts of *cis*
15 and *trans* decene-4 and decene-3, together being 95% of the total C₁₀ fraction. Similarly, the trimer fraction predominantly contained four internal olefins having a single branched alkyl chain. The composition of the higher oligomer fractions was more difficult to determine in
20 detail, but all these fractions have in common that olefins different from internal R₁-CH=CH-R₂ olefins are present in not more than trace amounts. Assuming response factors linearly correlating with the number of carbon atoms, the dimer over trimer and trimer over tetramer ratios in the
25 final reaction product were calculated to be 0.96 and 0.26, respectively.

- 18 -

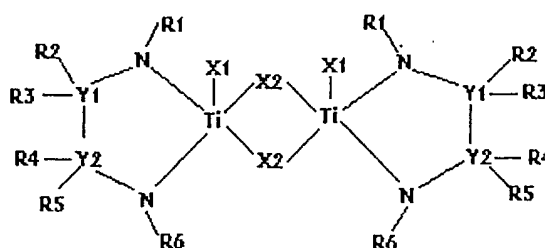
C L A I M S

1. Process for the oligomerization of one or more
olefinically unsaturated monomers comprising three or more
carbon atoms, at least one of these monomers consisting of
a C₃ to C₃₀ aliphatic mono-olefin, which process comprises
5 reacting the olefinically unsaturated monomer(s) under
oligomerization conditions in the presence of an effective
amount of a catalyst system based on

(a) a titanium bisamide compound of general formula (I) or
its dimer of general formula (II)



(I)



(II)

wherein:

Y¹ and Y² independently represent Si, Ge or Sn;

- 19 -

X^1 and X^2 independently represent a substituted or unsubstituted hydrocarbon group, in which one or more of the carbon atoms may be replaced by a Si atom, while in formula (I) X^1 and X^2 may also independently represent hydrogen or halogen or together form a ring structure; and

R^1 , R^2 , R^3 , R^4 , R^5 and R^6 independently represent hydrogen, halogen or a substituted or unsubstituted hydrocarbon group;

Q represents a neutral Lewis base; and
m is 0 or 1;

(b) one or more activating cocatalysts selected from the group consisting of

(i) compounds of formula U^+Z^- , wherein U^+ represents a cation capable of reacting irreversibly with one or more of the substituents X^1 and X^2 of the compound of formula (I) or (II) and Z^- represents a compatible non-coordinating anion comprising at least one boron atom; and

(ii) neutral strong Lewis acids comprising at least one boron atom; and optionally, but in any event if in the compound of formula (I) or (II) at least one of X^1 and X^2 represents halogen:

(c) one or more aluminium alkyls or alumoxanes.

2. Process as claimed in claim 1, wherein the process comprises reacting one or more C_3 to C_{30} aliphatic mono- α -olefins.

3. Process as claimed in claim 1 or 2, wherein the titanium bisamide compound is a compound of formula (I).

4. Process as claimed in any one of claims 1-3, wherein Y^1 and Y^2 represent Si.

- 20 -

5. Process as claimed in any one of claims 1-4, wherein X^1 and X^2 are selected from hydrogen, halogen, C_1 - C_5 alkyl, phenyl, 4-alkylphenyl and benzyl.

6. Process as claimed in any one of claims 1-5, wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are the same or different and are selected from hydrogen, C_1 - C_5 alkyl, trimethylsilyl, C_5 - C_8 cycloalkyl, phenyl and benzyl.

7. Process as claimed in any one of claims 1-7, wherein the cocatalyst is a compound of formula U^+Z^- , wherein U^+ represents a quaternary ammonium cation and Z^- represents a borate anion of formula $[B(R^8)_4]^-$, wherein the groups R^8 independently represent hydrogen or halogen-substituted or unsubstituted C_1 - C_{10} alkyl, C_5 - C_8 cycloalkyl, phenyl, C_7 - C_{15} alkylaryl or C_7 - C_{15} arylalkyl groups.

8. Process as claimed in claim 7, wherein U^+ is dimethylanilinium or tri(n-butyl) ammonium and Z^- is tetrakis (pentafluorophenyl) borate.

9. Process as claimed in any one of claims 1-8, wherein the catalyst system is based on components (a) and (b) in a molar ratio in the range of from 0.1:1 to 5:1 and component (c), if present, is used in such amount that the molar ratio between the aluminium in component (c) and the Ti in component (a) ranges from 10:1 to 10,000:1.

10. A mixture of homo-oligomers of propylene obtainable by the process of any one of claims 1-9, which mixture comprises oligomers of propylene based on up to 20 propylene molecules, wherein at least 50 mole% of the oligomer chains have a terminal vinyl group.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/06739

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C2/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 52631 A (MONTELL TECHNOLOGY COMPANY BV) 21 October 1999 (1999-10-21) claims -----	1-10

☐

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *I* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *8* document member of the same patent family

Date of the actual completion of the international search

29 August 2002

Date of mailing of the international search report

05/09/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Geyt, J

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 02/06739

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 10 (in part)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 10 (in part)

Present claim 10 relates to a mixture defined by reference to a desirable characteristic or property, namely the concentration of oligomers with a terminal vinyl group in the product. The claims cover all the mixtures having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such mixtures. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the mixtures by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the mixtures obtained in the examples.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/06739

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9952631	A	21-10-1999	
		AU 3813299 A	01-11-1999
		WO 9952631 A1	21-10-1999
		EP 1073521 A1	07-02-2001
		US 6372684 B1	16-04-2002
		US 2002035219 A1	21-03-2002

